

## PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

## Herbicidal Compositions

We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to herbicidal compositions, particularly a herbicide-paraffin wax composition, to methods of preparing such compositions and methods for inhibiting the growth of weeds on cultivated land.

Certain tests have shown that many selective herbicides are effective and rapid-acting weed killers when used in conventional compositions for weed killing before emergence of the crops, but tend to lose weed killing effectiveness rapidly or tend to be injurious to the crop if they are applied to the soil or are present in the soil in concentrations necessary for weed killing, after the crops start to grow. Commercial herbicides heretofore have usually been supplied as spray solutions or emulsions in various liquid solvents or carriers such as kerosene, stoddard solvent, aromatic hydrocarbons and chlorinated hydrocarbons. Other forms comprise emulsifiable oil concentrates containing up to 75% of the herbicide in a somewhat volatile liquid and granular powders comprising an inert solid material such as clay impregnated with the herbicide. Some of the liquid compositions are not suitable for dissolving some of the herbicides and the oil solvents have been found to increase the herbicidal effect in killing weeds but also to inflict serious damage to the crops, particularly if such oils are not sufficiently volatile to evaporate entirely. The impregnated inert solid composition is more persistent than the volatile oil compositions but has serious disadvantages in cost of production, separating, handling and distributing.

[Price 4s. 6d.]

It has now been found that improved herbicidal action can be obtained over a longer period of time with less damage to the crops by using a herbicidal composition comprising a suspension in water of finely divided particles of solid paraffin wax containing a herbicide and a wax-soluble dispersing agent or a dispersing agent in admixture with a compound which renders the dispersing agent wax-soluble.

Aqueous suspensions of the wax/herbicide composition are prepared by dissolving or dispersing a herbicide in a molten paraffin wax, preferably one having a melting point between 122 and 150°F, adding to the molten mixture from 1 to 10 weight % based on the total weight of the aqueous suspension of a wax-soluble dispersing agent or a dispersing agent in admixture with a compound which renders the dispersing agent wax-soluble, slowly adding the resultant solution or dispersion to warm water at a temperature from 10 to 20°F above the melting point of the wax, homogenizing the resultant aqueous suspension and cooling the resultant homogeneous aqueous suspension below the melting point of the wax.

The molten paraffin wax into which the herbicide is dissolved or dispersed is preferably about 10 to 20°F above its melting point. The homogenizing of the aqueous suspension is preferably carried out in a colloid mill or homogenizer which is capable of comminuting the herbicide-containing wax particles to a size of about 0.5 to 100 microns, preferably 0.5 to 10 microns. The resulting aqueous concentrate suspension preferably contains about 0.1 to 10 parts by weight of wax for each part by weight of the herbicide, depending on the control desired. The aqueous suspension may preferably contain about 30 to 70 wt. % water. The homogenized aqueous concentrate has a milky appearance.

If desired, the wax particles containing the

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herbicide may be separated from the water and applied as a dry powder, preferably after mixing with a solid, inert finely divided powder as a diluent.

- 5 In the preparation of the desired suspensions of solid wax particles containing the dissolved or dispersed herbicide, ingredients and processing steps are used which avoid forming a gel or liquid-in-liquid emulsion.  
10 Therefore, fats or oils which are fatty acid esters that tend to absorb water are not present in any significant amount, such as to cause water absorption or gelling of the paraffin wax particles.

- 15 The paraffin wax may be obtained by well-known commercial methods which generally include congealing of the wax solids in a petroleum fraction and separation of the congealed wax solids from the liquid hydrocarbons as by centrifuging and filtering. The crude wax is treated to lower the oil content as by sweating or by deoiling with solvents. The paraffin waxes include petroleum wax known as slack wax which may contain up to about 35% of oil and refined waxes.

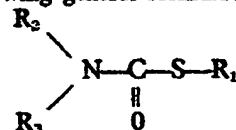
- 25 The wax-soluble dispersing agents which may be used for obtaining the suspension of the paraffin wax in water are substances that are known in the art as surfactants. These surfactants include, for example, monostearate esters of sorbitan, other esters of polyhydric alcohols, alkylaryl polyethers, and other surface active agents which serve to hold the solid wax particles in suspension. Water-soluble dispersing agents such as morpholine may also be used together with a solubilizer such as a fatty acid to render the dispersing agent wax soluble to form a suspension which may be considered a fast-breaking system due to the high volatility of the morpholine which evaporates after the dispersion is applied to the ground. The dispersing agents are preferably hydrophobic in character to avoid the retention or absorption of water in the wax herbicide particles when in suspension or after application.

- 45 The paraffin wax suspensions prepared in this manner are found to be much more effective than oil/water emulsions carrying the herbicides and are distinctive in several respects. The suspended paraffin wax particles containing the herbicide do not form a gel which has a tendency to absorb water. By the gradual addition of the molten wax containing

the herbicide to the warm water, there is no phase inversion and the herbicide remains in the wax particles which are suspended in the water. The suspension is made homogeneous and stable by use of a colloid mill, and finally the suspended solid wax particles remain suspended in the aqueous medium as discrete solid particles.

The wax-herbicide compositions may contain any herbicide, but it is specially suitable for use with the so-called selective herbicides designed to prevent or inhibit the growth of weeds without affecting the main crop. Such herbicides will vary in accordance with the crop to be grown on the land to which the material is applied.

Examples of these selective herbicides are: the alkyl thiolcarbamate of herbicides having the following general formula:



wherein  $R_1$ ,  $R_2$  and  $R_3$  are alkyl radicals having 1 to 5 carbon atoms. These alkyl radicals may be identical or different. Methods for synthesizing such alkyl-substituted esters of thiolcarbamic acid are described in U.S. Patents 2,913,324/5/6/7/8; other selective herbicides are the aryloxy compounds containing two to three chlorine substituents in the aryloxy group which is joined to an alkanic acid radical, such as acetic acid or propionic acid, and ester derivatives of these compounds. Examples of such compounds are 2,4-dichlorophenoxy acetic acid, its ester derivatives, and the compounds 2-(2,4,5)-trichlorophenoxy acetic acid or propionic acid and their ester derivatives. Principally, the relatively low volatility ester derivatives, such as the butoxy ethanol, propylene glycol monobutyl ether, and isoctyl alcohol esters of 2-(2,4,5)-trichlorophenoxy propionic acid are of high value for weed control in grain crops, such as wheat or barley, since these compounds are harmless to animals when present in low concentrations on the food crops.

Among the alkyl-thiolcarbamate herbicides are the following compounds which are given their chemical name and abbreviated name with an indication of the position of the alkyl groups in the general structural formula.

TABLE I

## THIOCARBAMATE HERBICIDES

Chemical Name	Abbreviated Name	Structure
Ethyl N, N-di-n-propyl thiocarbamate	EPP	$R_1=\text{ethyl}$ $R_2=R_3=\text{n-propyl}$
n-Propyl N,N-ethyl-n-butyl thiocarbamate	PEB	$R_1=\text{n-propyl}$ $R_2=\text{ethyl}$ $R_3=\text{n-butyl}$
n-Propyl N,N-di-n-propyl thiocarbamate	PPP	$R_1=R_2=R_3=\text{n-propyl}$
Butyl N,N-di-n-propyl thiocarbamate	BPP	$R_1=\text{n-butyl}$ $R_2=R_3=\text{n-propyl}$
Ethyl N,N-di-n-butyl thiocarbamate	EBB	$R_1=\text{ethyl}$ $R_2=R_3=\text{n-butyl}$
n-Propyl N,N-diethyl thiocarbamate	PEE	$R_1=\text{n-propyl}$ $R_2=R_3=\text{ethyl}$
Isobutyl N,N-diethyl thiocarbamate	IEE	$R_1=\text{isobutyl}$ $R_2=R_3=\text{ethyl}$
n-Amyl N,N-diethyl thiocarbamate	AEE	$R_1=\text{n-amyl}$ $R_2=R_3=\text{ethyl}$

Some of the above specific compounds have been found acceptable for use on feed crops, e.g. alfalfa, potatoes, beans, safflower, and flax (especially EPP), and for tomatoes and sugar beets (particularly PEB). With improved control, these herbicides are indicated to be attractive for use on other crops such as cotton, sugar cane, rice, asparagus, peas, corn, clovers, tobacco, onions, peppers, peanuts, lima beans, and spinach.

A typical wax suspension having a thiocarbamate herbicide dissolved in the wax phase is as follows:

12.5%	Thiocarbamate Herbicide (equivalent to 1 lb./gal.)
20.0%	Wax (130°F. Melting Point) (equivalent to 1.6 lbs./gal.)
67.5%	Water + Dispersing Agents
100.0%	

Such wax-herbicide concentrates are normally diluted for use at the rate of 1 to 6 gallons of concentrate to 40 gallons of water. This gives a resulting suspension containing from 0.3 to 1.9% of the active thiocarbamate herbicide and 0.5 to 3.0% wax.

The application rate for the cutback or diluted concentrate was in the range of 40

to 100 gallons per acre. This application rate gives a resulting lay-down or application rate of 1 to 6 pounds of the active herbicide per acre and 1.6 to 9.6 pounds of wax per acre.

Details of the scientific methods used in actual field tests of the herbicide on various crops for evaluating the wax-herbicide compositions, will be described in the following examples. In these tests, compositions of the herbicide in oil/water emulsions, on dry granular solids, and incorporated in wax suspensoid particles using slow-breaking and fast-breaking dispersing agents were used. In some of the tests, the oil or wax to herbicide ratio of 6:5 was used, and in others, the ratio of 4:5. The liquid preparations were applied in water using a sprayer delivering 40 gallons per acre. A number of the tests were made with incorporation of the laid-down material into the soil; others were made without doing so. In all the treatments, the comparisons were made with the same rates as expressed in terms of active ingredients per acre. The formulations were applied to randomized plots for proper statistical observation.

## EXAMPLE 1

The herbicide, butyl N,N-di-n-propyl thiocarbamate (BPP), was evaluated for pre-

emergence weed control in growing Thaxter baby lima beans and Clark soybeans. One wax composition contained 25% of this herbicide (BPP), 2.5% Span 60 (sorbitan monostearate), 2.5% Tween 60 (polyethoxy sorbitan monostearate), 0.15% Triton B-1956 (modified phthalic glycerol alkyd resin), 20% wax and 47.85% water in the concentrate as a slow-breaking suspension ("Span," "Tween" and "Triton" are registered Trade Marks). The fast-breaking system contained the same amount of herbicide and wax with 4.0% morpholine, 2% stearic acid, 0.15% Triton B-1956 and 1.0% of Triton X-45 (isooctyl phenyl polyethoxy ethanol).

Examination of the plots about one month after applying the herbicidal compositions and planting showed that the wax formulations were four to five times more effective than the standard formulations which did not have the herbicide in fine wax particles. The wax suspension formulations were about ten times as effective against broad-leaved weeds as the other formulations, and about three times more effective against grasses. Although there was somewhat higher early injury to the soybean seedlings, this was later outgrown. Such injury occurred mainly when incorporating the sprayed herbicide into the soil. The test indicated that lower amounts of herbicide could be used with the wax compositions and that incorporation into the soil could be eliminated. The effectiveness of the wax compositions against broad-leaved weeds was outstanding.

#### EXAMPLE 2

Various compositions of ethyl N,N-di-n-propyl thiocarbamate were used in tests on strawberries, corn and soybean plots for weed control and crop tolerance. In the corn experiment, the rates of herbicide applications were 3 and 5 pounds of active herbicide per acre. Ratings on weed control and crop injury were made periodically. The comparative effects are summarized as follows.

The wax compositions of this herbicide (BPP) effected greater weed control with decreased injury to the strawberry transplants than an oil emulsion of the same herbicide. There was less injury than that imparted by the herbicide on clay granules.

Improved weed control was obtained on the corn plots with substantially no crop injury in using the wax composition. The wax composition in which a slow-breaking dispersing agent was used gave somewhat better results when incorporated in the soil.

On the soybean crop plot, the wax compositions of the herbicide were as effective as herbicides not dispersed in wax for control of broad-leaved weeds after 38 days, and about two to four times as effective after 76 days with somewhat less crop injury.

#### EXAMPLE 3

Compositions of n-propyl N,N-ethyl-n-butyl thiocarbamate (PEB) were tested as in preplanting treatments on spinach at rates of 3 and 5 pounds of herbicide per acre. One composition was a conventional type with a volatile oil carrier, a second was with a high-boiling naphthenic hydrocarbon oil carrier, and a third was with an aqueous suspension of wax particles containing the herbicide according to the invention. Plantings of spinach were made 1, 4 and 7 days after herbicidal applications, and observations of the test plots were made 30 and 50 days later.

The tests showed that planting of the spinach seeds was safe and that better than adequate weed control was obtained, preferably with a longer delay for planting. The wax composition and heavy naphthenic oil composition were better than the standard composition with a more volatile hydrocarbon oil. The naphthenic oil used in the naphthenic oil composition was a selected naphthenic fraction containing hydrocarbons having above 18 carbon atoms per molecule. There was some superiority in crop safety when the wax composition was used.

In this particular test, there were indications that the low volatility naphthenic (cycloparaffinic) oil could be used together with the paraffinic wax in making improved compositions of the PEB herbicide. This naphthenic oil boiled in the range of 300° to 490°F. at 10 mm. pressure.

For the purpose of testing the wax compositions containing the aryloxy compounds, wax herbicide suspensions were prepared as shown in Table II.

TABLE II

## WAX FORMULATIONS CONTAINING ARYLOXY HERBICIDE

Herbicide: Propylene Glycol Monobutyl Ether Ester of 2-(2,4,5)-Trichlorophenoxy Propionic Acid.

## Composition, Wt. %

Herbicide	35.2	35.2
Paraffin Wax (190°F. Melting Point)	20.0	20.0
Span 60 (sorbitan monostearate)	2.0	—
Tween 60 (polyethoxy sorbitan monostearate)	2.0	—
Stearic Acid	—	1.5
Morpholine	—	3.0
Triton X-45 (isooctyl phenyl polyethoxy ethanol)	—	0.75
Triton B-1956 (modified phthalic glycerol alkyd resin)	0.15	0.14
Water	43.65	44.4
pH	4.9	9.8

A number of wax suspensions were given actual field tests for comparison with commercially available herbicides of the same "2,4,5-T" type. Each of the formulations was diluted with water to be sprayed on wheat and barley crops at rates of 1/8, 1/4, 1/2 and 1 lb. of active herbicide in 40 gallons of spray liquid per acre. Each application was replicated four times. The application was made after the crops were about 6 to 8 inches in height for postemergence weed control. The crops were rated at regular intervals and it was noted that the wax suspension formulations exhibited better weed control on all types of weeds and yet did not injure the grain crop as much as the standard commercial emulsion formulations.

Of particular concern in growing wheat and barley are weeds such as dog fennel which, if uncontrolled, will practically obliterate the desired crop, or at least stunt its growth drastically. In addition to this harmful effect, even a small amount of dog fennel among wheat and barley crops will reduce the value of the harvested crops. The reason for this is that dog fennel produces a daisy-like flower which has a bad odour. On har-

vesting the grain crop, this "stink daisy," as it is often called, is also cut and mixed with the kernels of grain and imparts an undesirable odour and taste. Such contamination reduces the value of the crop. Since the wax suspension particle formulations are more effective against such weeds as dog fennel, this advantage is of real value. The weed control tests are summarized as follows.

In comparing the wax-suspension applications with the commercial emulsion applications at the same rate of 1/2 lb. of the herbicide per acre, it was noted that the emulsion gave only about 50% weed control and stunted the crops slightly. At a higher concentration of 1 lb. of the active herbicide per acre, the wax suspension formulations gave complete weed kill with no crop injury, whereas the commercial oil emulsion of the herbicide formulation gave poor control with some crop injury.

From a large number of tests such as described with the various herbicides, there was an indication that these herbicides dissolved in the wax and remained in the small solid wax particles suspended in the water to give the desired controlled herbicidal activity with

low crop injury. These herbicides evidently are not leached out from the wax particles when homogenized in water containing dispersing agents, such as morpholine-fatty acid combinations or Tritons. The water spray solutions of the wax compositions containing the herbicides have been noted to form a thin film of the wax particles having a particle size in the range of about 0.5 to 100 microns on a glass surface, such as obtained in using an Eppenbach colloid mill in dispersing the wax solution of the herbicide in water.

The paraffin wax used in the composition is not in itself significantly herbicidal. Therefore, the compositions are surprisingly effective in weed killing power compared to the currently available oil compositions at any interval, before planting or after planting. The wax compositions have the additional advantage of giving greater persistency in weed killing after planting and starting of growth.

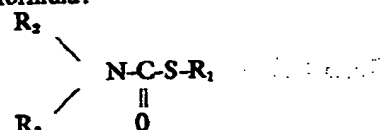
While the present invention has been particularly described with reference to the thiolcarbamate and halogenated aryloxyalkanoic acid herbicides in small solid wax particles, it is to be understood that various other herbicides may be used together in such wax compositions insofar as the substances do not detract from the desired advantages set forth. In using the compositions for post emergence control, other herbicides may be added which are compatible with the wax compositions if the particular crops are not adversely effected by such added herbicides. The wax compositions of the herbicides may be mixed with various solid fillers which are to be mixed with the soil or which are to be placed on the soil, e.g. sawdust, peat moss, vermiculite, sand, clay, and other granular substances.

#### 40 WHAT WE CLAIM IS:—

1. A method for preparing an aqueous suspension of a finely divided wax composition containing a herbicide comprising dissolving or dispersing a herbicide in a molten paraffin wax, adding to the molten mixture from 1 to 10 weight % based on the total weight of the aqueous suspension of a wax-soluble dispersing agent or a dispersing agent in admixture with a compound which renders the dispersing agent wax-soluble, slowly adding the resultant solution or dispersion to warm water at a temperature from 10 to 20°F. above the melting point of the wax, homogenizing the resultant aqueous suspension and cooling the resultant homogeneous aqueous suspension below the melting point of the wax.

2. A method as claimed in claim 1 wherein the herbicide is an alkyl thiolcarbamate or a di- or tri-chloroaryloxyalkanoic acid or an ester thereof, said alkyl thiolcarbamate having the

general formula:—



wherein  $R_1$ ,  $R_2$  and  $R_3$  represent alkyl groups containing from 1-5 carbon atoms.

3. A method as claimed in claim 2 wherein the herbicide is 2,4-di-chlorophenoxy acetic acid or 2-(2,4,5)-trichlorophenoxy acetic or propionic acid, or esters thereof.

4. A method as claimed in claim 3 wherein the herbicide is the propylene glycol monobutyl ether ester of 2-(2,4,5)-trichlorophenoxy propionic acid.

5. A method as claimed in claim 2 wherein the herbicide is ethyl N,N-di-n-propyl thiolcarbamate or n-propyl N,N-ethyl-n-butyl thiolcarbamate.

6. A method as claimed in any of claims 1-5 wherein the aqueous suspension of wax, herbicide and wax-soluble dispersing agent or dispersing agent in admixture with a compound which renders the dispersing agent wax-soluble is homogenized by passing said aqueous suspension through a colloid mill.

7. A method as claimed in any of claims 1-6 wherein the wax particles suspended in water have a particle size of from 0.5-100 microns.

8. A method as claimed in any of claims 1-7 wherein the paraffin wax has a melting point between 122° and 150°F.

9. A method as claimed in any of claims 1 to 8 wherein the suspension contains from 30-70% water.

10. A method as claimed in any of claims 1 to 9 wherein 1 part by weight of a herbicide is dissolved or dispersed in 0.1 to 10 parts by weight of wax.

11. A herbicidal composition comprising a suspension in water of finely divided particles of solid paraffin wax containing a herbicide and a wax-soluble dispersing agent or a dispersing agent in admixture with a compound which renders the dispersing agent wax-soluble.

12. A herbicidal composition comprising finely divided particles of solid paraffin wax containing a herbicide and a wax-soluble dispersing agent or a dispersing agent in admixture with a compound which renders the dispersing agent wax-soluble.

13. A herbicidal composition comprising a solid inert finely divided powder admixed with finely divided solid paraffin wax particles containing a herbicide and wax-soluble dispersing agent or a dispersing agent in admixture with a compound which renders the dispersing agent wax-soluble.

14. A method for inhibiting the growth of

weeds on cultivated land comprising treating the land with finely divided particles of solid paraffin wax containing a herbicide and a wax-soluble dispersing agent or a dispersing agent in admixture with a compound which renders the dispersing agent wax-soluble, or a suspension of such particles in water, prior to or after the emergence of the main crop.

15 5  
10 15. A method for preparing an aqueous suspension of a finely divided wax composition containing a herbicide substantially as herein described.

16. A herbicidal composition according to claims 11, 12 or 13 substantially as herein described.

17. A method for inhibiting the growth of weeds on cultivated land according to claim 14 substantially as described in any of the Examples.

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